Synthesis of a novel indium–nitrogen cage compound; molecular structure of $[(Np)In\{\mu\text{-}(NH)_2C_6H_4\}]_4$ (Np = CH_2CMe_3)

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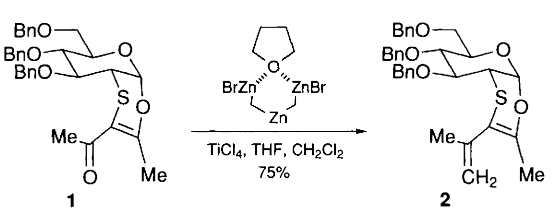
Reaction of $C_6H_4(NH_2)_2$-1,2 with $In(Np)_3$ (Np = neopentyl = CH_2CMe_3) affords the tetrameric compound $[(Np)In\{\mu\text{-}(NH)_2C_6H_4\}]_4$, which contains five-coordinate indium centres having square-pyramidal geometry and an overall approximate tetrahedral symmetry.

Chelating ligands containing donor atoms of group 15 elements have been used to stabilize electrophilic group 13 elements.[1–3] The relevant studies have shown the diversity of such compounds characterized by varied degrees of oligomerization and complex coordination of the metal centres. In this regard, five-coordinate organometallic compounds of group 13 elements were limited to those using macrocyclic ligands.[4] For example, most five-coordinate indium compounds usually have distorted bipyrimidal[5–7] geometry, while fewer are known to have square-pyramidal geometry.[8–10] In a recent study, we demonstrated that the independent reactions of $AlMe_3$ and $GaMe_3$ with $C_6H_4(EH_2)_2$-1,2 (E = N, P) in a 2 : 1 ratio produces four-coordinate tetrametallic compounds, $[(Me_2M)_4\{(\mu\text{-}PH)_2(C_6H_4)\}_2]$ (M = Al, Ga), through alkane elimination.[11] In a related study, reactions of sterically demanding primary amines with $AlMe_3$ resulted in isolation of several novel large aggregates of aluminium compounds but similar reactions with $GaMe_3$ led to C–H activation forming a 'cyclometallated' compound.[12] Only recently, Roesky and co- workers[13] reported the first organometallic cubane compounds for GaN and InN systems, $(C_6F_5NMMe)_4$ (M = Ga, In), from the reaction of MMe_3 with $C_6F_5NH_2$. Herein, we discuss the formation of the novel twelve-membered cluster $[(Np)In\{\mu\text{-}(NH)_2C_6H_4\}]_4$ (Np = neopentyl = CH_2CMe_3).



Scheme 1 *Reagents and conditions*: i, toluene, reflux, 24 h, –8HNp

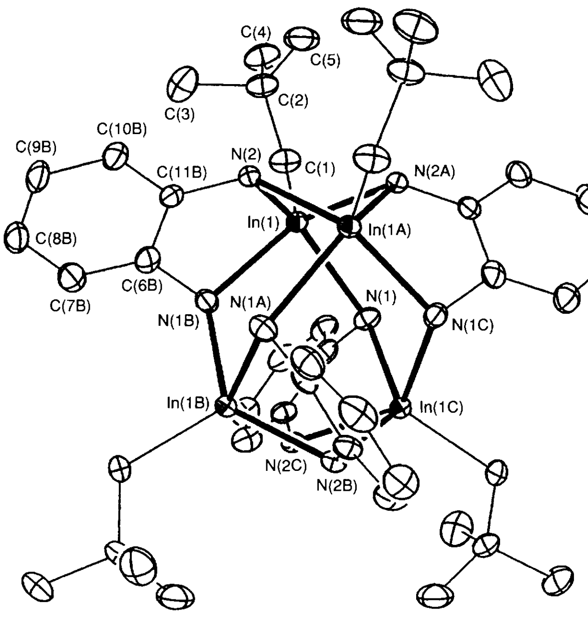


Fig. 1 Molecular diagram (30% probability ellipsoids) of $C_{44}H_{68}In_4N_8$ **1**, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): In(1)–C(1) 2.166(7), In(1)–N(2) 2.270(6), In(1)–N(1) 2.290(6), In(1)–N(1B) 2.259(6), In(1)–N(2A) 2.285(6), N(1)–C(6) 1.453(10), N(2)–C(11B) 1.400(8), C(11)–N(2C) 1.400(8), In(1)···In(1A) 3.2675(10); C(1)–In(1)–N(1B) 119.0(3), C(1)–In(1)–N(2) 119.4(3), N(1B)–In(1)–N(2) 73.8(2), C(1)–In(1)–N(2A) 111.2(3), N(1B)–In(1)–N(2A) 129.0(2), N(2)–In(1)–N(2A) 74.5(2), C(1)–In(1)–N(1) 107.7(3), N(1B)–In(1)–N(1) 89.1(2), N(2)–In(1)–N(1) 132.5(2), N(2A)–In(1)–N(1) 83.9(2), C(6)–N(1)–In(1) 103.4(4), C(6)–N(1)–In(1C) 108.4(4), C(11B)–N(2)–In(1) 112.0(5), C(11B)–N(2)–In(1A) 125.2(4), In(1)–N(2)–In(1A) 91.7(2), In(1C)–N(1)–In(1) 121.7(3).

The reaction† of $In(Np)_3$ with $C_6H_4(NH_2)_2$-1,2 in a 1 : 1 ratio resulted in the isolation‡ of **1** as shown in Scheme 1.

Compound **1** is formed *via* alkane elimination and is isolated as colourless crystals which are sparingly soluble in aromatic solvents and slowly decompose in the presence of air. The X-ray structural analysis§ of **1** reveals a tetramer with overall

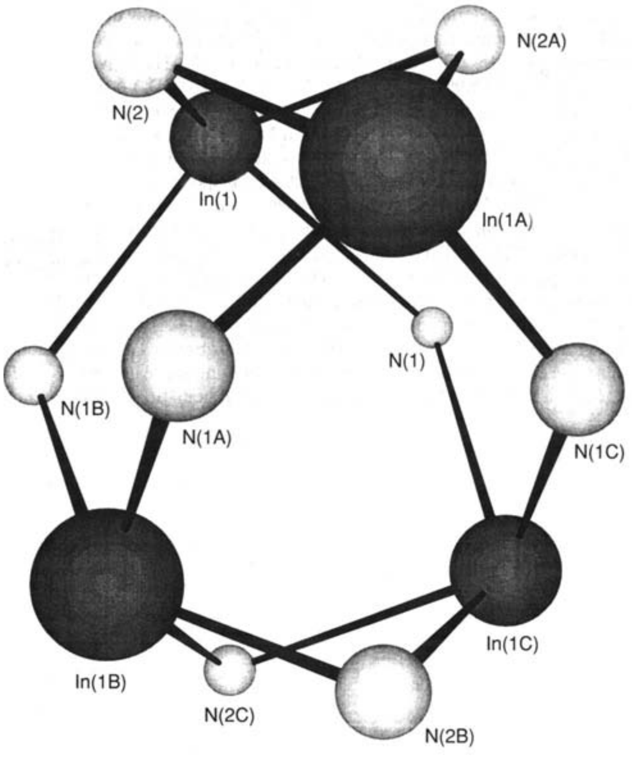


Fig. 2 Molecular diagram of the InN core in $C_{44}H_{68}In_4N_8$ **1**

tetrahedral symmetry (Figs. 1 and 2), composed of square-pyramidal indium centres with similar In–N distances. The In(1)/In(1A) and In(1B)/In(1C) pairs have closer In···In interactions than the other pairs. This is a consequence of the members of the pair being doubly bridged by the N(2)/N(2A) and N(2B)/N(2C) atoms. The N···N separation between N(2)/N(2A) and N(2B)/N(2C) is 2.74 Å, which is shorter than distances between N(1A)/N(1B) and N(1)/N(1C) (3.19 Å). All four In atoms are physically and chemically equivalent, but there is no fourfold overall symmetry. The In–N distances are in the range 2.259(6)–2.290(6) Å [average 2.276(6) Å] and are slightly longer than the cubane ($(C_6F_5NInMe)_4$), with an average In–N bond length of 2.20 Å.[13] This can be rationalized since the indium atoms in **1** are five- rather than four-coordinate as in $(C_6F_5NInMe)_4$. In conclusion, alkane elimination works smoothly to yield **1** and we will now investigate whether aluminium and gallium can form large clusters with $C_6H_4(NH_2)_2$-1,2.

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Footnotes

† *General considerations*. All manipulations were performed using general Schlenk and dry box techniques. Solvents were dried over Na/K alloy and distilled under dinitrogen prior to use. A literature method was used to prepare $In(CH_2CMe_3)_3$;[14] $C_6H_4(NH_2)_2$-1,2 was purchased from Aldrich and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a GE-300 spectrometer operating at 300 and 75.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$-spectra were referenced to $SiMe_4$ by using the residual protons or carbons of deuteriated benzene at δ 7.15 or 128, respectively. Melting point (uncorrected) was obtained with a Thomas-Hoover Uni-melt apparatus and the capillary was flame sealed under argon. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Mass spectral data was collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. The IR spectrum was acquired for a KBr pellet on a BOMEM Michelson MB-100 FTIR spectrometer. X-Ray crystallographic data were obtained at 25 °C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation.

‡ *Synthesis of* **1**. Inside the Dri-Lab, 0.71 g (2.17 mmole) of $In(Np)_3$ was combined with 0.24 g (2.17 mmole) of $C_6H_4(NH_2)_2$-1,2 in a 250 ml Schlenk flask and *ca*. 40 ml of toluene was added to the mixture. The mixture was refluxed for 24 h. The volume of resultant pale yellow solution was decreased by *ca*. 20 ml *in vacuo* and left undisturbed. X-Ray quality crystals of **1** were deposited in the bottom of flask within 24 h. Yield, 90% based on $In(Np)_3$; mp 245 °C. Anal. Calc. (Found) for $C_{44}H_{68}In_4N_8$: C, 45.23 (45.35); H, 5.87 (5.99); N, 9.59 (9.54%). ^1H NMR (C_6D_6) δ 6.82 (8 H, m, C_6H_4), 6.66 (8 H, m, C_6H_4), 3.14 (8 H, s, NH), 0.96 (8 H, s, In–CH_2), 0.82 (36 H, s, CMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 142.8, 140.5, 121.2, 119.0, 118.4, 114.3 (s, C_6H_4), 34.3 (s, CMe_3), 31.3 (s, In–CH_2), 30.9 (s, CMe_3). Mass spectral data (EI mode): peak at *m/z* 293 corresponding to [$\frac{1}{4}$M + H]. IR (cm^{-1}): 3282, 3310, 3375 [ν(N–H)]; 1629w and 1584s cm^{-1} [δ(N–H)].

§ *X-Ray structural solution and refinement*. A suitable crystal was mounted in a thin-walled capillary and sealed with silicone grease under an argon atmosphere and then flame sealed. The unit-cell parameters were obtained by least-squares refinement of the angular setting of 24 reflections ($20 < 2\theta < 25°$). Preliminary photographic evidence indicated a tetragonal crystal system with $4/m$ Laue symmetry. The systematic absences in the diffraction data were consistent for *I*-centring and the following space groups: $I4$, $I\bar{4}$, $I4/m$, $I422$, and $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$, $I4/mmm$. An *E*-statistic suggested a non-centrosymmetric space group. The presence of tetrahedral molecular symmetry, the absence of mirror-plane symmetry in the placement of neopentyl and C_6H_4 groups, and Z = 2, eliminated all of the space group options except for $I\bar{4}$. The solution in $I\bar{4}$ produced a chemically reasonable structure and computationally stable refinement. The structure was solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. A semi-empirical absorption correction was applied. The structure was refined as a racemic twin with a 70:30 ratio of enantiomeric lattice. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL(5.3) program libraries.[15]

Molecular diagrams showing the solid state conformation and atom numbering schemes of **1** and the core of **1** are presented in Figs. 1 and 2, respectively, with selected interatomic distances and angles listed in the figure captions.

Crystal data: $C_{44}H_{68}In_4N_8$ **1**, *M* = 1168.34, colourless plate, 0.4 × 0.4 × 0.18 mm, tetragonal, space group $I\bar{4}$, $a = b = 10.194(2)$, $c = 23.4380(10)$ Å, $U = 2435.6(7)$ Å^3, $Z = 2$, $D_c = 1.593$ g cm^{-3}, $F(000) = 1168$, Mo-Kα = 0.71073 Å, 2024 reflections collected with 1911 independent; refinements converged to $R = 0.0340$ ($wR2 = 0.0894$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/287.

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